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PHOTOELECTROCHEMICAL FABRICATION OF GRATINGS IN SiC

by

M. M. Carrabba, J. Li, J. P. Hachey and R. D. Rauh

EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

and

J. Wang

Department of Materials Science and Engineering
North Carolina State University, Raleigh, NC 27695

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Photoelectrochemical etching has been demonstrated as a means for generating high resolution patterns in Silicon Carbide. Both CVD and epitaxial (on Si) SiC were used. Liquid electrolytes containing either fluoride or ethylene diamine were found to promote smooth photoanodic dissolution, without passivation. Very low anodic dark currents permitted the highest degree of spatial selectivity in the epitaxial material, although patterned photoetching of CVD-SiC could be achieved under high light intensity. Diffraction gratings were demonstrated by defining the grating structure in photoresist on the electrode surface, then photoetching the spaces exposed to the electrolyte.

SiC has considerable significance as a substrate for gratings in the vacuum ultraviolet and x-ray wavelengths due to its high reflectance in these regions. Additionally, it has a high degree of stability against thermal degradation and radiation damage, making it a choice material for high power laser optics. Because of the extreme hardness of SiC,

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it is difficult to fabricate gratings by ruling. The photoelectrochemical method demonstrated here is a simple one-step technique that should be adaptable to large area CVD and epitaxial SiC substrates that are available commercially.

Photoelectrochemical Fabrication of Gratings in SiC

M.M. Carrabba, J. Li, J.P. Hachey, and R.D. Rauh

EIC Laboratories, Inc., 111 Downey Street, Norwood, MA 02062

Y. Wang

Department of Materials Science and Engineering
North Carolina State University, Raleigh, NC 27695

Introduction - There has been considerable recent interest in photoelectrochemical etching as a rapid and economical method for fabricating diffraction gratings in semiconductor materials. Most of this work has been directed toward III-V semiconductors, since photoanodic dissolution occurs smoothly in a variety of electrolytes due to the high degree of solubility of the oxidation products. SiC is a semiconductor of considerable significance as a substrate for gratings in the vacuum ultraviolet and X-ray spectral regions, due to its high reflectance. Additionally, it has a high degree of stability against thermal deformation and radiation damage, making it an excellent candidate for use with high intensity radiation associated with high power lasers and synchrotron light sources. It is difficult to rule gratings into SiC due to its extreme hardness, although gratings have been produced by ion etching using a photoresist mask. Optical blanks are most commonly made from CVD SiC. However, epitaxial SiC on Si is being reported in sizes suitable for optical and electro-optical components.

There have been only a few reports of photoanodic dissolution of n-SiC. The semiconductor is generally regarded as being anodically unstable in aqueous solution. Gleria and Memming [1] and Morisaki et al. [2], using single crystals of the 6H crystallographic modification, have indicated that the anodic process is accompanied by the formation of a passivating SiO_2 layer in electrolytes based on H_2SO_4 or NaOH, while passing reference was made to higher photocurrents and less passivation in aqueous HF electrolytes. Brander and Boughey [3] have described the anodic (dark) etching of both n and p-SiC 6H single crystals in HF electrolytes of various strengths. They observed electropolishing in 2-5N HF solutions at current densities up to 10 A/cm^2 in a process that consumed approximately 8 equivalents/mole.

Experimental - Epitaxial SiC on Si were prepared at North Carolina State University and NASA-Lewis by previously described methods [4][5]. The epitaxial layers were 4-6 μm thick predominantly β SiC, and the doping levels were approximately 1 x 10^{17}/cm^3. CVD SiC was obtained from CVD Corp., Woburn, MA, and was predominantly the 6H (hexagonal) form. The material was not intentionally doped, but was weakly n-type.

The SiC electrodes were first washed and degreased in acetone, then methanol. An ohmic contact was made by rubbing with Ga-In eutectic. Epitaxial SiC had to be contacted on the top surface in order to get photon limited photocurrents. The contact was shielded from the electrolyte using epoxy resin. The CVD substrates were contacted on the back side and mounted in electrode holders that also served as a potting device for polishing. The electrode surface was lapped and polished to a mirror finish with diamond pastes of decreasing grit size down to 0.1 μm.

Electrochemical measurements were made with a potentiostat and function generator, a standard calomel (SCE) reference electrode and a Pt gauze cylindrical counter electrode surrounding the SiC working electrode. The light source was a 100W Xe arc lamp. A monochrometer and a phase sensitive detection were employed to determine the wavelength dependence of photocurrent, which was corrected for variation in source intensity.

Results and Discussion - Current-voltage curves were recorded for epitaxial and CVD SiC electrodes in the dark and under broadband illumination. The epitaxial material showed photon-limiting photocurrents with negligible dark current (<10 μA/cm^2 at 1.2V). The CVD electrodes displayed dark current on the order of 0.1 to 0.3 mA/cm^2 at 1.2V, and photocurrent that increased exponentially with applied voltage. The dependence of photocurrent on wavelength is compared for the two types of electrodes in Figure 1. The onset at 520 nm is probably indicative of the presence of cubic β-SiC which has an indirect bandgap at 2.2 eV (564 nm) [6]. The lack of response at longer wavelengths for the epitaxial SiC shows that absorption by the Si substrate is not contributing to the photocurrent. Even on a normalized scale, the CVD electrode response curve is shifted to higher energies, possibly indicating the presence of higher bandgap hexagonal 6H SiC components. However, the high dark currents and lack of photon-limiting currents in CVD SiC suggests that the space charge region is poorly developed and the Fermi level is pinned near the conduction band. This would result in a low efficiency of separation of electron-hole pairs produced at longer wavelengths in the SiC bulk.

Several electrolytes were examined for their ability to sustain photoanodic dissolution of SiC without passivation of the electrode surface. In these experiments, the electrode was biased at 1.2V (SCE) and the dark current, then photocurrent monitored under illumination of 3 W/cm^2 from a focused Xe source. High intensities could be used to increase the ratio of photocurrent over dark current in the CVD material to greater than 50:1 at >1V. Photocurrents of >2 mA/cm^2 could be sustained for at least an hour without significant decreases for acidic electrolytes containing fluoride (e.g., 1-5M HF and 0.1-1.0M ammonium bifluoride), and in 0.5M ethylene diamine/0.1M KCl. Neutral electrolytes (e.g., 1M KCl) showed rapid passivation. Scanning electron micrographs of a n-SiC surface photoelectrochemically etched in aqueous electrolytes revealed the evolution of a porous layer, probably SiO_2, coating a smoother etched underlayer. This indicates that "passivation" really signifies the electrolyte permeability of undissolved reaction products.

Preliminary experiments were carried out to etch a lithographically defined grating structure in both epitaxial and CVD SiC materials. The SiC substrates were cleaned and pretreated with a photoresist adhesion promoter. Substrates were then spin coated with Shipley 1400-31 positive photoresist and processed according to the manufacturer's instructions. Grating patterns were generated with a cyclic mask having a periodicity of 100 cycles/mm and a line/space ratio of 1. The patterned electrodes showed few defects when examined under a metallurgical microscope.

Photoelectrochemical etching of the patterned electrodes was carried out in the nonpassivating electrolytes determined previously. Etching of the structures was typically conducted at 1V vs. SCE using the high intensity source, resulting in photocurrents of 2 to 4 mA/cm^2. The major limitation in all experiments was the eventual delamination of the photoresist. Nevertheless, etched periodic structures approximately 1 micron deep were obtained, shown in SEM photographs in Figure 2. An underlying irregular morphology is noticeable in the CVD material, possibly delineating polycrystalline grain boundaries. A rough microstructure at the 0.1 to 0.5 μm level was observed for all etched gratings related to local variations in the dissolution and porosity of SiC oxidation products.

In conclusion, these experiments clearly demonstrate the feasibility of photoelectrochemical etching of deep microstructures in n-SiC. Although no attempt was made to optimize the process, it seems that a judicious choice of masking materials and electrolytes will be necessary to enhance the uniformity and smoothness of the final structures. In addition, maskless etching by projection of images such as interferograms should be possible. Epitaxial SiC appears ideal for replication of interferograms because of the low light intensities involved and hence the requirement for very low dark current.

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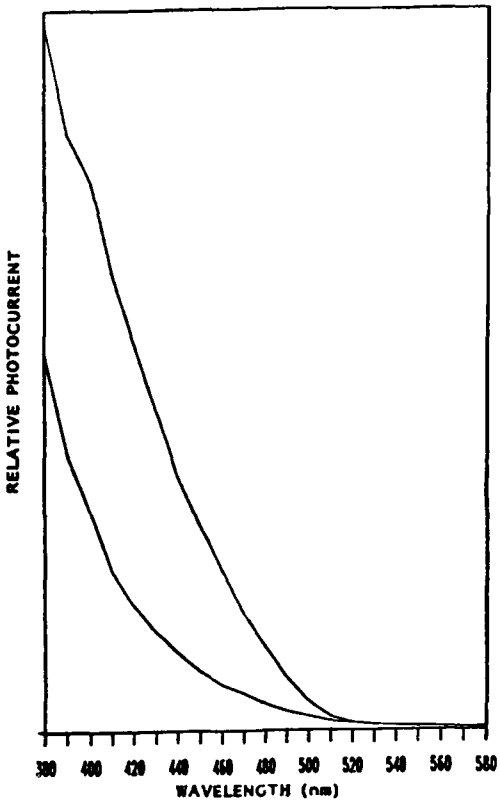

Fig. 1. The photocurrent vs. wavelength response curves for CVD (bottom) and EPI (top). The photoetchant was HF.

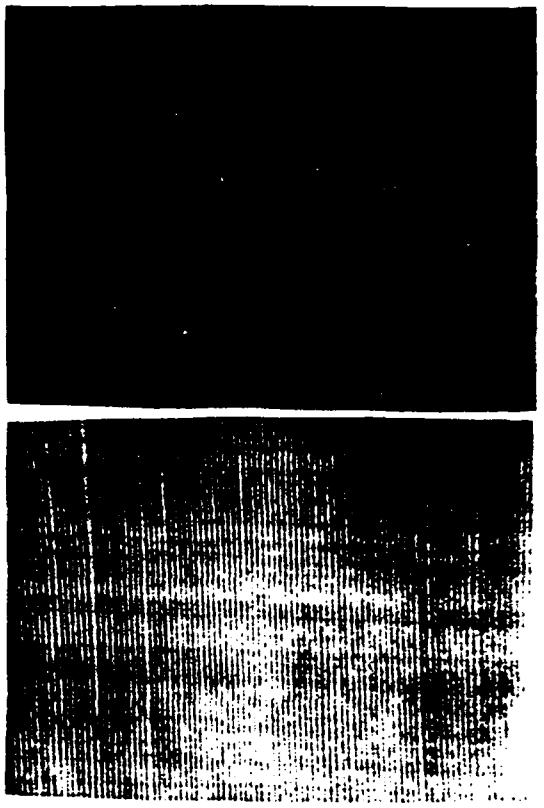

Fig. 2. Scanning electron micrographs (50X) of grating structures photoelectrochemically etched in CVD (top) and EPI (bottom) SiC.

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